SPIN-VALVE EFFECT IN A Ni-C_{60}-Ni DEVICE

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ABSTRACT

We present here the results of theoretical calculations on the spin-valve effect in a Ni-C_{60}-Ni device. The magnitude of the junction magnetoresistance (JMR) is found to be significantly large for the device, which makes it a promising candidate for realistic applications in molecular spintronics. The exploration of the origin of the observed spin-valve effect in the Ni-C_{60}-Ni system will be discussed.

1. INTRODUCTION

Spintronic devices are attractive for many potential Army applications ranging from memory storage and magnetic field sensors to quantum computing devices. The central theme of spintronics is to actively control and manipulate spin degrees of freedom in solid state systems. The prototypical structure of a spin valve consists of two magnetic layers bridged by a non-magnetic spacer: F1/N/F2. In such a device, the conduction electrons experience a lower resistance (R) when the relative orientation of the magnetizations in two ferromagnetic layers F1 and F2 are aligned in parallel (PL, *on* state) than in anti-parallel (AP, *off* state). This is the so-called spin-valve effect or magnetoresistive effect. It is characterized by JMR=$(R_{AP}-R_{PL})/R_{PL}$ in a junction.

The discovery of giant magnetoresistive effect (MR>10%) has led to the present generation of read/write heads for magnetic data storage impacting on a multibillion industry. However, in order to achieve the industrial target of one Tb/in^2, a further device miniaturization is required, with the ultimate goal of producing atomic scale ultrasensitive sensors used as the magnetic read/write heads. In this line of inquiry, spintronics starts to converge with the burgeoning field of molecular electronics, in the sense that we are now beginning to consider the use of individual molecules as the non-magnetic spacer in a spin valve. The advantages are that the size of molecules is usually in the sub-nanoscale; identical molecules can be manufactured cheaply and easily in industry quantities, and can provide reliable and uniform performance.

To this day, however, only very few rigorous studies have been done in this field (Zwolak *et al*., 2002; Pati *et al*., 2003; Wei *et al*., 2004; Rocha *et al*., 2005; He *et al*., 2006), and as a result, many open questions remain. Especially the role of the molecule and the effect of the molecule-electrode interface need to be fully understood before one can develop molecular spintronic devices for specific applications. In this paper, we will discuss results from our first-principles calculations on the spin-polarized electron transport in a two-terminal Ni-C_{60}-Ni device where the fullerene molecule is bonded by atomic-scale ferromagnetic nickel contacts (Fig. 1). There are several advantages of choosing C_{60} as the spacer. Firstly, the mass-production of C_{60} is well established. Secondly, C_{60} is structurally very stable. Last but not least, it is well known that the C_{60} molecule can be electronically active as either an electron acceptor or an electron donor with a band gap as small as 1.7 eV.

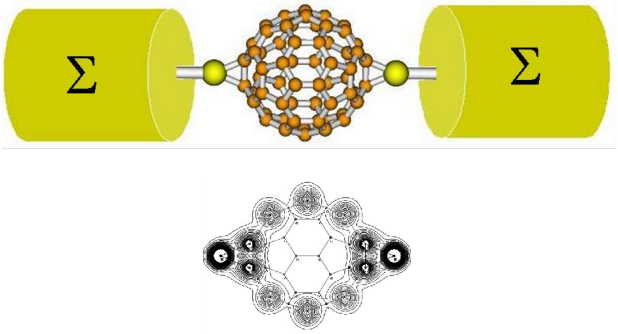

Fig. 1 A schematic illustration of a Ni-C_{60}-Ni molecular device. Top: The left/ right contact region is modeled by a Ni atom and the rest of the semi-infinite electrode is a Ni bulk reservoir, described theoretically by an effective self-energy Σ. Bottom: A slice of the charge density plots of the center scattering region is shown for the bridge site over a C=C double bond (B66).

2. COMPUTATIONAL DETAILS

We begin with the construction of a two-terminal molecular electronic device by coupling the C_{60} molecule to the ferromagnetic Ni electrodes. Our main interest in

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the present study lies in understanding of the electronic and transport properties of Ni-C_{60}-Ni for the cases of the parallel (PL) and anti-parallel (AP) spin configurations of the system.

The spin-polarized electronic transport calculations have been performed for Ni-C_{60}-Ni using density functional theory (DFT) (Frisch *et al*., 1998) in conjunction with the Green's function-based Landauer-Bütticker multi-channel formalism (Landauer, 1989; Büttiker, 1986; Datta, 1995). In such a molecular junction, the metal-molecule interface is expected to play a critical role in determining the current-voltage (*I-V*) characteristics. To investigate the role of the metal-molecule interface, the chemical bonding and its contribution to transmission function will be discussed in detail with respect to the binding sites of Ni on C_{60}.

The Green's function-based Landauer-Bütticker formalism (employing the coherent scattering together with the no spin-flip scattering assumptions) was used to calculate the electron transport properties in a low bias regime for both PL and AP spin configurations of the system. The Ni atom at each side of C_{60} is assumed to be at the end of a contact which is connected to a Ni electrode reservoir. Since Ni bulk is a ferromagnetic material having unbalanced spin-up (↑) and spin-down (↓) electrons near its Fermi level, the tunneling channels for spin-up (↑) and spin-down (↓) electrons are explicitly separated.

The total current in such a system can be obtained by a summation of the contributions from both the spin-up ($I^{\uparrow}$) and the spin-down ($I^{\downarrow}$) electrons. The current-voltage (*I-V*) relation is evaluated as follows:

$$I^{\uparrow(\downarrow)} = \frac{2e}{h}\int_{-\infty}^{\infty} dE\, T^{\uparrow(\downarrow)}(E,V)\left[f(E-\mu_1) - f(E-\mu_2)\right] \quad (1)$$

where μ_1 and μ_2 are the electrochemical potentials in the two contacts under an external bias V, $f(E)$ is the Fermi-Dirac distribution function. $T(E,V)$ is the electron transmission function which can be calculated from a knowledge of the molecular energy levels and their coupling to the metallic contacts. $T(E,V)$ is an important intrinsic factor in transport properties, which describes the quantum mechanical transmission probabilities for electrons with energy E under a bias V. As reported in other molecular systems, no significant shift in molecular spectra has been seen in the presence of low applied bias (Heurich *et al*., 2002; Pati *et al*., 2003), suggesting one does not expect a significant change in transmission function in the low bias regime that we have considered here either. We have not included the bias induced effect in this study.

3. RESULTS AND DISCUSSION

C_{60} has a high symmetry of icosahedra I_h consisting of *twelve* regular pentagons and *twenty* regular hexagons. All the C atoms are equivalent with sp^2 hybridization and each C atom is bonded to another three C atoms with two single bonds and one double bond. The C_{60} molecule offers a variety of sites for atoms bonded to the C_{60} cage externally. We have performed first principle calculations based on the Dmol program package (Delley, 1990, 2000) to find the site-preference of a Ni atom bonded externally to C_{60}. The B66 site (i.e. the bridge site over a C=C double bond) is found to be the most favorable site for Ni, relative to the B56 site (i.e. the bridge site over a C–C single bond), the H5 site (i.e. the hole site above the center of a pentagonal ring of C atoms), and the H6 site (i.e. the hole site above the center of a hexagonal ring of C atoms). This is consistent with an earlier study reported by Alemany *et al.* (Alemany *et al.*, 2001) using the quenching MD simulation approach.

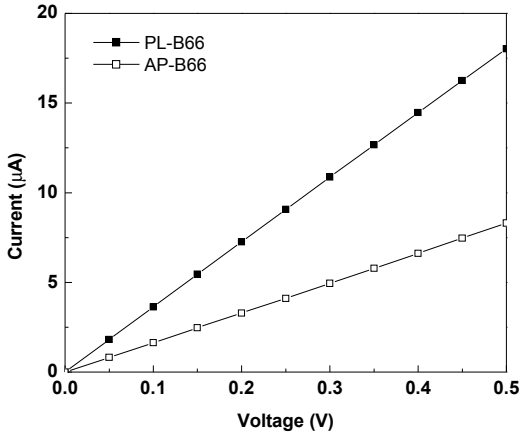

Fig. 2 The current-voltage (*I-V*) curves for parallel (PL) and anti-parallel (AP) spin configurations of Ni-C_{60}-Ni with Ni binding at the bridge site over a C=C double of C_{60}─B66.

The current-voltage (*I-V*) characteristics have been calculated for both PL and AP spin configurations with Ni binding at the B66 site of C_{60}, as shown in Fig. 2. A significant spin valve effect – higher PL current than AP current, is observed in this system. Moreover, our electronic structure calculations reveal that the ground state (the lowest in energy) of such a system has an anti-parallel spin configuration (*off* state). The natural anti-parallel spin alignment eliminates the need for applying a local magnetic field to obtain an *off* state, which would be a formidable task in a real-world application otherwise. The *I-V* curves are then used to calculate the junction magnetoresistance (JMR) with respect the external bias voltage (Fig. 3). And it shows a relatively small variation

with bias. The magnitude of JMR is found to be significantly large for the device, with a value around 110%. It is close to the maximum experimental value of 80% reported by Ralph's group in Cornell (Pasupathy *et al*., 2004).

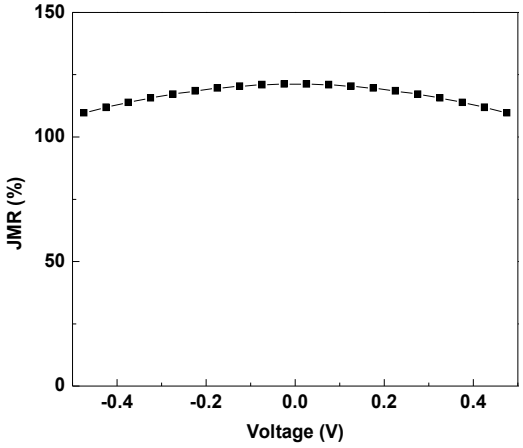

Fig. 3 The junction magnetoresistance (JMR) of Ni-C_{60}-Ni with Ni binding at the B66 site of C_{60}.

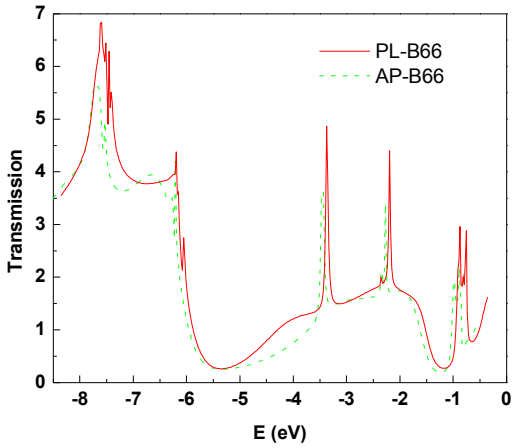

Fig. 4. Transmission functions for (a) parallel (PL) (solid line) and (b) anti-parallel (AP) (dashed line) spin configurations of Ni-C_{60}-Ni with Ni binding at the B66 site of C_{60}.

In order to trace the physical origin of this spin-valve effect in C_{60} mediated spin-polarized electron transport between two ferromagnetic electrodes, we have plotted the transmission functions (T) for the Ni-C_{60}-Ni system in Fig. 5 (a) and (b) for both PL and AP spin configurations. The Ni atom is taken to be bonded externally at the B66 site of the C_{60} molecule. We note here the similarity in the shape of T except a small shift to lower energy for the AP case relative to the case of PL. It suggests that T reflects the intrinsic characteristics of the molecule despite the differences intrigued by the different spin configurations. However, a bump appears in the near Fermi region (~ -4 eV) in the case of PL spin configuration, which contributes to a larger current. The feature of this broad peak is currently under investigation.

It is probably due to the interaction between the molecule and electrodes and can often be attributed to the bonding states. The occurrence of this peak (the one instantly below -4 eV) is clearly seen in the α (spin-up) state molecular spectra in the PL configuration. It is the α-HOMO of the extended Ni-C_{60}-Ni molecule complex, which makes the sole contribution to the electron transmission near E_f. Nonetheless, this feature is not found in either the spin-down (β) states in PL configuration or the spin-up and spin-down (α and β) states in AP configuration, where the states below LUMO are only composed of metallic states from the Ni contact.

As a result of this, the tunneling current (obtained through Equation (1)) is significantly higher in the PL case than those in the AP case for both binding sites, which is clearly shown in Fig. 2. In the low bias region (< 0.5 V), a linear response is observed for the PL spin configuration, showing an ohmic-like behavior. However, a closer look at the differential conductance (not shown here) suggests a slightly different trend in the variation of conductance with respect to external bias voltage due to the different variation of transmission function in the vicinity region of E_f.

In the AP case, a linear response in I-V curve in the low bias regime is well preserved. However, the differential conductance dI/dV is significantly decreased compared to the PL alignment of spins between the two contacts.

4. CONCLUSIONS

In summary, density functional theory together with the Landauer-Bütticker formalism is used to calculate the spin-polarized electron transport through a C_{60} molecule coupled to ferromagnetic Ni electrodes. The tunneling current is found to be highly polarized. A significant spin-valve effect is observed with a JMR of 110%, which is also observed in experiments among the few experimental reports on the spin-valve effect in magnetic-organic systems (Xiong *et al*., 2004; Petta *et al*., 2004; Pasupathy *et al*., 2004). The difference in the transmission function for parallel (PL) and anti-parallel (AP) spin configuration is clearly revealed. A further study of the chemical bonding at the interface of Ni-C_{60}-Ni may shed light on the physical origin of the spin-valve effect.

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